Parametric Study on the Reduction of m-chloronitrobenzene by using H_2S-rich MEA

Thesis submitted by

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Under the Guidance of

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CERTIFICATE

This is to certify that the thesis entitled "**Parametric Study on the Reduction of m-chloronitrobenzene by using H_2S-rich MEA**", submitted by Gajendrakumar (212CH1071) in partial fulfillment for the requirements of award of Master of Technology in Chemical Engineering at National Institute of Technology, Rourkela under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree.

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ABSTRACT

In the present study, metachloronitrobenzene was reduced to a value added chemical metachloroaniline, which is used as a intermediate for pharmaceuticals, agriculture chemicals...etc. the reactions carried out in an organic solvent, toluene using Liquid-Liquid-Solid mode with phase transfer catalyst, Amberlite IR 400. The conversion as well as reaction rate of m-CNB were studied by the effect of different parameters such as speed of agitation, reaction temperature, catalyst loading, concentration of reactant, sulfide concentration and concentration of MEA. The reactions were carried out in a fully baffled mechanically well agitated glass reactor of capacity 250ml for 8 hrs. operation. The selectivity of m-CA was found out to be 100% at all time. The overall rate of reaction was found to be proportional to the catalyst loading and concentration of reactant, and square of the sulfide concentration. The reactions were found to be kinetically controlled with apparent activation energy of 56.16 KJ/mol. The generalized mechanism of the reaction was studied.

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LIST OF ABBREVIATIONS

DEA	Diethanolamine
DIPA	Diisopropanoloamine
GLC	Gas Liquid Chromatography
LLSPTC	Liquid-Liquid-Solid Phase Transfer Catalysis
m-CA	meta-chloroaniline
m-CNB	meta-chloronitroabenzene
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
OVAT	One variable at a time
ppm	Parts per million
ppmv	Parts per million by volume
PTC	Phase Transfer Catalysis
TEA	Triethanolamine
TPC	Tri Phase Catalyst

CHAPTER 1

INTRODUCTION

1. Introduction

This chapter involves a broad overview of the present research work and its vitality. It includes introduction to the sources of hydrogen sulfide, need to treat it off and recovery. It also envisages upon the conventional process used in the industries, the objectives of this study and a note on the structure and organization of the thesis.

1.1 Sources of Hydrogen Sulfide

Sour gas (which is natural gas) can contain up to 90% hydrogen sulfide, whereas small amount of hydrogen sulfide occurs in petroleum. Volcanoes and some hot springs (as well as cold springs) emit some H_2S, where it is probably due to the hydrolysis of sulfide minerals, i.e.

$$MS + H_2O \rightarrow MO + H_2S$$

Hydrogen sulfide also present naturally in well water, as a result of the action of sulfate-reducing bacteria which generate energy under low oxygen conditions by using sulfates to oxidize organic compounds or hydrogen and produces hydrogen sulfide as a byproduct.

10-12% of global H_2S emissions is due to human activities. However, the largest industrial route to H_2S is occurs in petroleum refineries by hydrodesulfurization process. The resulting H_2S is converted to elemental sulfur by the Claus process. Other sources of hydrogen sulfide include coke ovens, paper mills (using the sulfate method), and tanneries. H_2S arises where elemental sulfur comes in contact with organic material, at high temperatures (at about 450^0C).

In 2011, it was reported that the concentration of H_2S increases due to oil field practices, presented challenges such as "health and environmental risks, corrosion of wellbore, added expenses with regard to materials handling and pipeline equipment, and additional refinement requirements. The H_2S contents varies from 0.1ppm -15000ppm.

1.2 Need of Treatment of H_2S gas

Hydrogen sulfide is a highly toxic and flammable gas having range: 4.3–46%. It has high density than air, that’s why it tends to accumulate at the bottom of ventilated spaces. Although very pungent (like rotten egg) at first, which quickly deadens the sense of smell, so potential

victims may be unaware of its presence until it is too late. For safe handling procedures, a hydrogen sulfide material safety data sheet (MSDS) should be consulted.

Table 1.2 Standards of H_2S emissions

Occupational Exposure Limit (8 hrs. weighted avg.)	10 ppm
Public Exposure Limit (for general population)	0.006-0.03 ppm

Hydrogen sulfide is a broad-spectrum poison, that can poison several systems in the body, mostly on the nervous system. The toxicity of H_2S is comparable with that of hydrogen cyanide or carbon monoxide. It forms a complex bond with iron in the mitochondrial cytochrome enzymes, thus preventing cellular respiration.

H_2S is odiferous in nature, in the presence of water it is corrosive and poisonous in small concentrations too. Therefore, it should be removed completely from the gas streams before transport. As a result, specifications limit for the pipeline has given as the amount of H_2S to less than 0.25 g per 100 ft^3 of gas (Thomas, 1990).

The presence of H_2S in the refinery gas streams causes no. of detrimental problems in subsequent processing steps like corrosion of process equipment, deterioration and deactivation of the catalysts, undesired side reactions, increase in the process pressure requirements, increase in the gas compressor capacity, etc. (Hamblin, 1973).

Table 1.2: Effect of H_2S on Heath

Concentration in ppm	Observation and health effect
<1	Smells like rotten eggs
3-5	Very strong pungent smell
20-150	Nose and throat feel dry, eyes irritated, eyes symptoms may occur
150-200	blocked sense of smell (olfactory fatigue)
200-250	High irritation of nose, throat and lungs occurs, along with headache, nausea, vomiting and dizziness. Prolonged exposure causes fluid buildup in the lungs (pulmonary edema)
>250	Same symptoms as above but more severe. Death can be occur within 1 to 4 hrs. of exposure. Above 500 immediate loss of consciousness. Death is likely to be immediate.

1.3 Processes to remove H_2S from the stream gases

To meet the stringent environment regulation, the H_2S contents of the byproduct gas streams are brought down to a definite level before being used in further applications. There are various processes to remove and recover H_2S from the gas stream. Alkaline solution is used to remove H_2S since H_2S is acidic (weak acid) in nature. A strong alkaline solution like sodium hydroxide, however, forms irreversible chemical reaction products with H_2S and therefore can't be employed for the removal of H_2S from gas streams especially if the gas contains both H_2S and CO_2 where the conc. of CO_2 is >4% (Robin, 1999). This leads to the use of a weak alkaline solution like ammonia and alkanolamines for the removal and recovery of H_2S.

1.3(a) Ammonia-based Processes

Use of aqueous ammonia in elimination of H_2S (sometimes along with NH_3) from gas streams have been well experienced (Hamblin, 1973 and Harvey and Makrides, 1980). Gas streams containing both H_2S & NH_3 permit through a H_2S scrubber and an NH_3 scrubber in order. Stripped water is fed to the top of the NH_3 scrubber where it absorbs NH_3 from the gas. The subsequent NH_3 solution is then used as absorbent for H_2S in the H_2S scrubber. The H_2S-rich solution, is fed

to a deacidifier, which decomposes the ammonium sulfide to produce H_2S rich vapor and NH_3 rich liquor. The reactions occurring in the system comprised of ammonia, hydrogen sulfide, and water can be represented by the following equations (Scheme 1.1)

$$NH_3 + H_2O = NH_4OH$$
$$NH_3 + H_2S = NH_4HS$$
$$2NH_3 + H_2S = (NH_4)_2S$$

Scheme 1.1

The NH_3-based process has some notable advantages over amine-based process (Kohl and Nielsen, 1997) as: The NH_3-based process is mainly suitable for gas streams containing both H_2S & CO_2 (like hydrotreater off gas and coal gas), as simultaneous removal of NH_3 is noticeable in this process. Moreover, for the gas streams containing both H_2S and NH_3, the removal of both impurities could be done in a single step in the ammonia-based process however, alkanolamine-based process required two steps (NH_3 removal by water scrubbing followed by H_2S removal through the amine treating unit).

The rate of absorption of H_2S into aqueous NH_3 solution is rapid and depends upon the concentration of NH_3. Hence, with suitable NH_3 concentration at the interface, it is possible that the gas film resistance governs the rate of absorption of H_2S. On the other hand, absorption of CO_2 in weak alkaline solution like aqueous NH_3 is considered typical of a liquid film controlled system. When stream gases containing both H_2S and CO_2 are contacted with aqueous NH_3 solution, the absorption of H_2S is much more rapid than the CO_2. Another aspect is that in solution, the CO_2 is stronger acid than H_2S and at equilibrium conditions, process expected to be selective for CO_2. Therefore, by using aqueous NH_3, the selective absorption of H_2S or CO_2 is possible from the gas stream containing both H_2S and CO_2. By the use of spray column in combination with little contact time can lead to the selective absorption of H_2S from the gas mixture containing both CO_2 and H_2S. NH_3 has the advantage for such applications being essentially unpretentious by the presence of carbonyl sulfide (COS), carbon disulfide (CS_2) and hydrogen cyanide (HCN).

Despite these advantages, it has several disadvantages of this method as the ideal method for removing H_2S from gas stream. This is primarily because of a number of operational difficulties related with its implementation (Hamblin, 1973), such as:

- High partial pressure of NH_3 forces the scrubbing step be led with relatively dilute NH_3 solutions or at relatively high pressures or a separate water wash step after the NH_3 scrubbing step in order to remove NH_3 from treated gas stream.
- The use of dilute scrubbing solutions characteristically increases regeneration costs where the regeneration step is conducted at higher temperature than the scrubbing step.
- Another difficulty is with the regeneration of the rich absorbent solution withdrawn from the scrubbing step. Several regeneration techniques have been projected but they typically comprise the use of soluble catalysts such as hydroquinone and have problems such as contamination of the sulfur product with the catalyst, excessive formation of side products such as ammonium sulfate and thiosulfate and loss of scrubbing solution and catalyst during the periodic purges that required to remove side products from the system.
- Other difficulties have been associated with the recovery of the elemental sulfur from the regeneration step where it has been form a froth of sulfur, which must be skimmed off and filtered.

1.3(b) Alkanolamine-based Process

Alkanolamine-based process got wide commercial acceptance as the gas treating art because of its advantages of low vapor pressure i.e. high boiling point and ease of reclamation. The low vapor pressures of alkanolamines makes the operation suppler in terms of operating pressure, temperature, and conc. of alkanolamine in addition to the negligible vaporization losses.

Di-iso-propanolamine (DIPA) (Bally, 1961; Klein, 1970) is used to some extent in the Adip process, in the Sulfinol process and in the SCOT process for Claus plant tail gas cleansing. However, methyldiethanolamine (MDEA) is regularly displacing DIPA in these applications. Although MDEA was described by Kohl and coworkers at Fluor Daniel (Frazier and Kohl, 1950; Kohl, 1951; Miller and Kohl, 1953) as a selective absorbent for H_2S in the presence of CO_2 as early in 1950, its use in industrial processes has only become important in recent years. A somewhat different type of alkanolamine, 2-(2-aminoethoxy) ethanol, commercially recognized as Diglycolamine (DGA), was first suggested by Blohm and Riesenfeld (1955). This compound pairs the stability and reactivity of monoethanolamine with the low vapor pressure and viscosity of diethylene glycol. Therefore, it can be used in more concentrated solutions than monoethanolamine.

In addition to simple aqueous solutions of the mentioned alkanolamines, proprietary formulations comprising mixtures of the amines with various additives are broadly used. Formulated solvents are offered by Dow Chemical Company (GAS/SPEC), Union Carbide Corp. (Amine Guard and UCARSOL), Huntsman Corporation (formerly Texaco Chemical Company) (TEXTREAT), and BASF Aktiengesellschaft (Activated MDEA). Some of Dow's GAYSPEC and UOP's Amine Guard formulations are basically corrosion inhibited MEA and DEA solutions. However, the most significant development in formulated solvents is the advent of tailored amine mixtures. These are based on MDEA, but contain other amines as well as corrosion inhibitors, foam depressants, buffers, and promoters blended for specific applications. They can be designed to provide selective H_2S removal, partial or complete CO_2 removal, high acid gas loading, COS removal, and other special features (Manning and Thompson, 1991; Pearce and Wolcott, 1986; Thomas, 1988: Meissner and Wagner. 1983; Meissner, 1983; Niswander et al., 1992). In general, it is considered that the hydroxyl group helps to reduce the vapor pressure and increases the water solubility, while the amino group provides the necessary alkalinity in water solutions to cause the absorption of acidic gases.

1.4 Sulfur recovery from H_2S

1.4(a) Claus Process:

H_2S is an insufferable substance that converted to non-toxic and useful elemental sulfur. It is patented by the scientist Carl Friedrich Claus in 1883. The multi-step Claus process recovers sulfur from the hydrogen sulfide. H_2S gas separated from the host gas stream using *amine extraction*, is fed to the Claus unit (Fig. 1.1), where it is converted in two steps:

Thermal Step: In this step**,** The H_2S-laden gas reacts in a substoichiometric combustion with air. This is done at high temperatures (about 1000 – 1400^{o}C) in a reaction furnace. Acid gases with no further combustible contents apart from H_2S are burned in burner by the following chemical reaction:

$$\mathbf{2H_2S + 2O_2 \rightarrow SO_2 + 2H_2O + S}$$

This is a highly exothermic flame free oxidation of hydrogen sulfide generating sulfur dioxide which reacts in subsequent reactions. The ratio of air to acid gas is controlled in such a

way that total 1/3 of all H_2S is converted to SO_2. This ensures a stoichiometric reaction for the Claus reaction in the 2nd step.

Catalytic Step: The reaction gases leaving the sulfur condenser are reheated to 200-350°C and fed to the series of catalytic converter and sulfur condenser where H_2S react with SO_2 to produce elemental sulfur.

$$\mathbf{2H_2S + SO_2 \rightarrow 3S + 2H_2O}$$

The catalyst used in the catalytic converter is normally either activated aluminum (III) or titanium (IV) oxide. Unavoidably a small extent of H_2S leftovers in the tail gas. This residual extent, with other trace sulfur compounds, is deal with in a tail gas unit. It gives overall sulfur recovery of about 99.8%, which is very notable. Sulfur is used to produce sulfuric acid, medicine, cosmetics, fertilizers and rubber products. Elemental sulfur is also used as a fertilizer and pesticide.

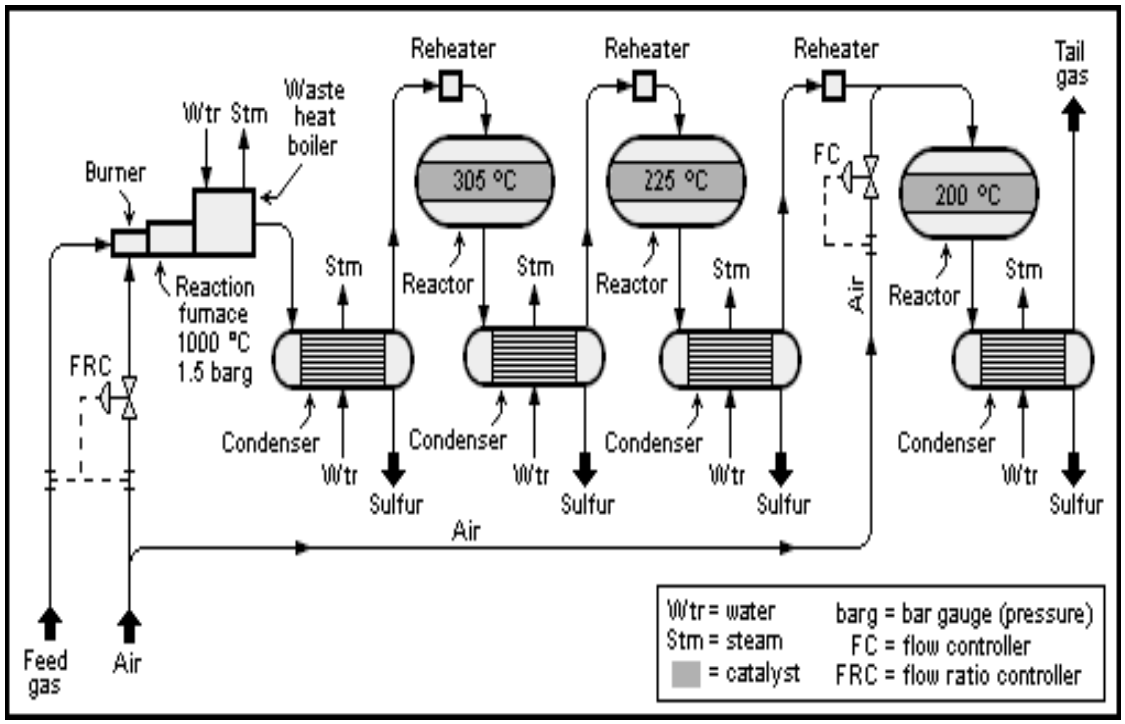


Fig.1.1: Process Flow Diagram of Claus Process

However, the Claus process has a number of inherent disadvantages (Plummer, 1994; Plummer and Beazley, 1986; Plummer and Zimmerman, 1986). For example:

- It operates at high temperatures.
- It requires exact process control over the ratio of oxygen to H_2S in the feed.

- The valuable hydrogen energy is lost in this process.
- It requires expensive pretreatment of the feed gas if CO_2 is present in high concentrations. At least a portion of the CO_2 must be removed from the byproduct gas by pretreatment before oxidizing the H_2S to maintain the efficiency of the oxidation process.
- The sulfur content of Claus process tail gas released to the atmosphere is generally too high to meet stringent environmental regulations.

To comply with these regulations, it is necessary to add more Claus stages and/or employ a separate tail gas cleanup process at great expense.

Process improvement

Recent developments in the Claus Process are:

Superclaus: A catalyst in the last reactor oxidizes H_2S to sulfur, avoiding formation of SO_2. Significantly higher conversions are obtained at modest cost.

Oxygen Claus: Mixing of combustion air with pure oxygen reduces the amount of nitrogen passing through the unit, which increases throughput.

Better Catalysts: catalyst provides higher surface area and macroporosity, therefor higher activities have been achieved.

Other Ways to Process Sour Gas

H_2S containing gas is incompatible for treatment using amine extraction because of high CO_2 levels. These streams offer themselves to process by so-called liquid redox processes such as CrystaSulf or SulFerox or ARI-LO-CAT. These processes use liquid solution containing oxidized iron instead of air. Numerous novel processes have been developed to separate hydrogen and sulfur both from H_2S. These are called H_2S Splitting Processes. Hydrogen is a valuable gas for the oil processing and for the production of ammonia and methanol.

1.5(b) Wet-oxidation LO-CAT Process

In this process, safe chelated iron catalyst is used to convert hydrogen sulfide to elemental sulfur. The iron catalyst is held in solution by organic chelating agents that wrap around the iron in a claw like style, preventing precipitation of either iron sulfide (FeS) or iron hydroxide

($Fe(OH)_3$). The hydrogen sulfide, absorbed in the alkaline, aqueous LO-CAT solution (pH 8.0-8.5), which is oxidized to elemental sulfur by reducing the iron ions from the ferric to the ferrous state. The reduced iron ions are then moved from the absorber to the oxidizer where the ferrous iron is reoxidized to ferric iron by atmospheric oxygen and absorbed into the LO-CAT solution, thus regenerating the catalyst.

1.5 Phase Transfer Catalysis

Phase transfer catalysts (PTC) are widely used to strengthen slow heterogeneous reactions involving an organic substrate and an ionic reactant, either dissolved in solvent (liquid-liquid) or present in solid state (solid-liquid). Phase transfer catalysis is an attractive technique for organic synthesis because of its advantages such as simplicity in operation, reduce utilization of organic solvent and raw materials, mild operating conditions and enhancement reaction rates aa well as selectivity. Phase transfer catalysis has 600 applications covering a wide spectrum of industries such as pharmaceuticals, agro-chemicals, perfumes, flavors, dyes, specially polymers, pollution control etc. in this work I have used liquid-liquid-solid (L-L-S) PTC, Amberlite IR 400 which can be separated by simple methods like filtration and can be reused. However, in L-L-S PTC, has some disadvantages such as loss of activity due to binding of catalyst on the solid surface, lower reaction rates due to intraparticle diffusion limitations and high primary cost of preparation.

Resin-Bound Phase Transfer Catalysts

Tomoi and Ford gave a term “polymer-supported” PTC to describe the PTC reactions occurring in the polymer phase. Resin-bound PTC catalysts include polymer- NR^{3+}, -PPh^{3+}, -SR^{2+}, -crown ether, -cryptand, -azacrown, -PEG, etc. In case of the ordinary PTC reactions using soluble catalysts, PTC reactions using resin-bound catalysts require both reactants diffuse to active PTC sites or the resin surface or to active sites inside the resin bulk phase for the intrinsic reaction rate limited reactions. These also imply that both reactants are required to diffuse and penetrate the stagnant outer layer of the liquid(s) (i.e., the Nernst layer) coating the resin particle as demonstrated by Tomoi and Ford (1981), known to have a slow intrinsic reaction rate, catalyzed by the styrene–divinylbenzene resin-bound tributylphosphonium catalyst. The resin-bound PTC catalysts generally consist of three elements, namely, the insoluble supporting cross-linked resin backbone, a spacer chain (optional), and the PTC functional group. Taking advantage of the huge amount of

available ion-exchange resins, most published studies on resin-bound PTC reactions use styrene–divinylbenzene and related resins.

1.5(a) Interfacial Mechanism of Phase Transfer Catalysis

Phase transfer catalysts (PTC) have the ability to carry one of the reactants as a highly active species for penetrating the interface into the other phase where the reaction takes place. It gives high conversion and selectivity for the desired product under mild reaction conditions. This type of reaction was termed "phase-transfer catalysis" (PTC) by Starks in 1971. Since then, several work has been done to investigate the applications, reaction mechanisms and kinetics of PTC.

Two mechanisms have been proposed for solid-liquid phase transfer catalysis (Starks and Liotta, (1978), Yadav and Sharma, (1981), Melville and Goddard, (1988), Naik and Doraiswamy, (1997)). One mechanisms is applicable where the inorganic salt holds substantial solubility in the solvent and the catalyst is unable to approach the solid surface closely. The second mechanism operates in cases where the inorganic salt is insoluble or very slightly soluble in the organic solvent and the quaternary catalyst can react directly with the solid surface to render the anionic species soluble. These phenomena are also referred to as homogeneous and heterogeneous solubilization (Melville and Goddard, 1988). A small quantity of aqueous phase in a solid (inorganic)-organic liquid phase leads to enhancements in reaction rates and this is termed as the omega phase.

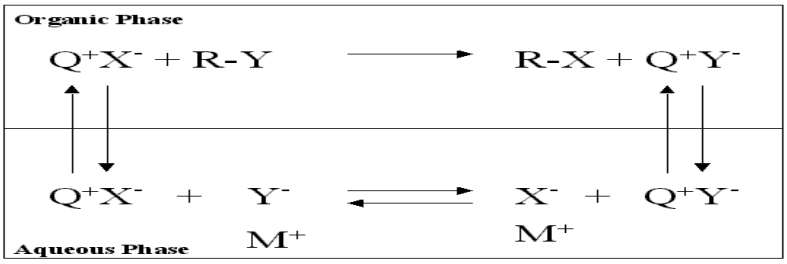


Fig.1.2: Mechanism of PTC

Two mechanisms, interfacial and extraction are used to clarify the liquid-liquid phase transfer catalysis based on the lipophilicity of the quaternary cation. The extraction mechanism, as suggested by Starks (1971), and by Starks and Liotta (1978), is applicable to catalysts that are not highly lipophilic or that can distribute themselves between the organic and the aqueous phase, such as benzyltriethylammonium, dodecyltrimethylammonium, and tetrabutylammonium salts. In the interfacial model, catalysts such as tetrahexylammonium and trioctylmethylammonium salts

remain entirely in the organic phase because of their high lipophilicity and exchange anions across the liquid-liquid interface (Dehmlow and Dehmlow, 1983).

In liquid-liquid-solid phase transfer catalysis (L-L-S PTC), the solid phase is the main reaction phase. The advantages of L-L-S PTC over normal PTC are: (i) increase in reaction rates by orders of magnitude; (ii) easier catalyst recovery and reuse; (iii) the reaction can be carried out in a continuous reactor by continuously separating the catalyst; (iv) better selectivity, hence the attendant difficulties of reduced activity and mechanical strength associated with liquid-liquid-solid (L-L-S) PTC can be avoided.

The wetting nature of support matters a great deal in LLSPTC (G.D. Yadav and S.S. Naik, 2004). The microporous resins have low specific surface areas and the polymeric chains shrink in a dry state or poor solvents. A macroporous polymer possessing high porosity which swells considerably would be a better choice as support for the PTC.

1.5(b) Liquid-Liquid-Solid Phase Transfer Catalysis

Liquid-liquid phase transfer catalysis (LLPTC) is the most widely synthesized method for solving the problem of the mutual insolubility of nonpolar and ionic compounds (Dehmlow 1993, Starks et al. 1994, Weber and Gokel 1977, Halpern 1997 and Goldberg 1992). Two compounds in immiscible phases are able to react because of the PTC.

However, processes using a two phase PT-catalytic reaction always encounter the separation problem of purifying thefinal product from the catalyst. Regen (1975) first used a solid-phase catalyst (triphasecatalyst (TC) or polymer-support catalyst), in which a tertiary amine was immobilized on a polymer support, in the reaction of an organic reactant and an aqueous reactant. From the industrial application point of view, the supported catalyst can be easily separated from the final product and the unreacted reactants simply by filtration or centrifugation. In addition, either the plug flow reactor (PFR) or the continuous stirred tank reactor (CSTR) can be used to carry out the reaction. The most synthetic methods used for triphase catalysis were studied by Regen and Beese (1975-79) and Tomoi and coworkers (1981-83). Another advantage of triphase catalysis is that it can be easily adapted to continuous processes was studied by Ragaini et al. (1986-90). Therefore, triphase catalysis possesses high potential in industrial scale applications for synthesizing organic chemicals from two immiscible reactants. Quaternary onium salts, crown ethers, cryptands, and polyethylene glycol have all been immobilized on various kinds of supports,

including polymers (most commonly methylstyrene-co-styrene resin cross-linked with divinylbenzene), alumina, silica gel, clays, and zeolites. Because of diffusional limitations and high cost, the industrial applications of immobilized catalysis (triphase catalysis) are not fully utilized. This unfortunate lack of technology for industrial scale-up of triphase catalysis is mainly due to a lack of understanding of the complex interactions between the three phases involved in such a system. In addition to the support macrostructure, the support microenvironment is also crucial in triphase catalysis since it determines the interactions of the aqueous and the organic phases with the PT catalyst immobilized on the support surface studied by Naik and Doraiswamy (1998). However, to date, few papers have discussed the microenvironment.

The effect of the internal molecular structure of the polymer support, which plays an important role in the imbibed composition, on the reaction rate has seldom been discussed. In addition to the reactivity, for a TC in an organic and aqueous solution the volume swelling, imbibed different solvent ratio, amount of active site, and mechanical structure of the catalyst must be considered. Hence, these complex interactions in the microenvironment must be solved in order to obtain a high reactivity of TC.

1.5(c) Mechanism of LLSPTC

In general, the reaction mechanism of the fluid–solid reactions involves: (1) mass transfer of reactants from the bulk solution to the surface of the catalyst pellet, (2) diffusion of reactant to the interior of the catalyst pellet (active site) through pores, and (3) intrinsic reaction of reactant with active sites. Triphase catalysis is more complicated than traditional heterogeneous catalysis, because it involves not merely diffusion of a single gaseous or liquid phase into the solid catalyst. Both organic reactant and aqueous reactant exist within the pores of the polymer pellet. For step (3), a substitution reaction in the organicphase and an ion-exchange reaction in the aqueous phase occurred. Diffusion of both the aqueous and organic phases within the solid support is important and various mechanisms have been proposed for triphase catalysis. However, each mechanism can only explain asingle reaction system. Naik and Doraiswamy (1998) discussed these mechanisms in their review paper.

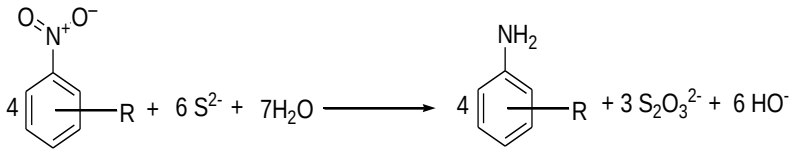
Tundo and Venturello (1979-82) proposed a mechanism for a TC system using silica gel as support to account for the active participation of the gel by adsorption of reagents.Telford et al. (1986) suggested an alternation shell model that requires periodical changes in the liquid phase

filling the pores of the catalyst. Schlunt and Chau (1986) from the same research group tried to validate this model using a novel cyclic slurry reactor, and indicated that only the catalyst in a thin shell near the particle surface was utilized. Tomoi and Ford (1981) and Hradil et al. (1988) reported that a realistic mechanism involves the collision of droplets of the organic phase with solid catalyst particles dispersed in a continuous aqueous phase. Svec"s model (1988) for transport of the organic reagent from the bulk phase through water to the catalyst particle has been developed in terms of emulsion polymerization. Because the triphase reaction involves not merely diffusion of a single phase into the solid support, the organic reaction take places in the organic phase and the ion-exchange reaction occurs in the aqueous phase. The catalyst support is usually lipophilic. The organic phase and aqueous phase fill the catalyst pores to form the continuous phase and the disperse phase, respectively. The interaction between quaternary salts as well as the organic phase and aqueous phase play a crucial role in promoting the triphase reaction rate.

1.6 Reduction of Nitroarenes

The reduction reaction of nitroarenes by negative divalent sulfur (sulfide, hydrosulfide, and polysulfides) is called Zinin reduction (Dauben, 1973). Sodium sulfide, sodium disulfide, and ammonium sulfide are commonly used in the Zinin reduction. The reaction, first used by Zinin in 1842 to prepare aniline from nitrobenzene, since it has been great importance in the preparation of aromatic amines. Even though catalytic hydrogenation process or iron reduction method has gained popularity commercially, the Zinin reduction method is still being applied with more sensitive compounds that would not be friendly with acid media and when selective reduction of polynitroarenes required.

The stoichiometry of the Zinin's reduction of nitrobenzene by aqueous ammonium sulfide is given by Dauben, in 1973 as shown below. This stoichiometry is also applicable for the reduction of nitroarenes by sodium sulfide (Bhave and Sharma, 1981; Pradhan and Sharma, 1992a; Pradhan, 2000; Yadav et al., 2003b, 2003c).



1.7 Present Work

The present work was undertaken to develop a substitute process (alternative to Claus or LO-CAT process) for better utilization of H_2S. The present work deals with the production of value-added chemicals utilizing the H_2S present in various byproduct gas streams obtained from different chemical industries. In accordance with the present process, value-added chemicals were produced from the H_2S-rich aqueous alkanolamine that could be obtained from scrubbing step of the corresponding alkanolamine-based process. In other words, the removal of H_2S was assumed to be done by conventional process. The present investigations are devoted to:

- Synthesis of m-chloroaniline using the H_2S- rich aqueous methanolamine under three phase (Liquid-Liquid-Solid) conditions in the presence of a phase transfer catalyst (PTC), Amberlite IR 400.
- Study the effect of process variables (stirring speed, catalyst loading, concentration of reactant, temperature, concentration of MEA, elemental sulfur loading) on the conversions of organic reactant (m-chloronitrobenzene) and selectivity of products.
- Establish a suitable mechanism or stoichiometry utilizing the effects of different parameters on the reaction rate and conversion, to explain the course of the reaction.
- Kinetic modeling of the above mentioned commercially important reactions and estimation of the model parameters.

CHAPTER 2

LITERATURE REVIEW

2. Literature Review

This chapter deals with the literature study associated to the use of alkanolamines as H_2S gas absorbent, Different methods of synthesizing Benzyl mercaptan and Dibenzyl sulfide, Use of various catalyst for the development of valuable products using the H_2S present in gases.

2.1 Removal of H_2S using Ammonium Hydroxide and Aqueous Alkanolamine

Kohl and Nielsen (1997) has been well documented the use of ammonium hydroxide for the removal and recovery of hydrogen sulfide from the gas streams.

Hamblin (1973) developed a process for removal of H_2S from gas streams using ammonium hydroxide for the production of ammonium hydrosulfide, which further oxidized to get an effluent stream containing ammonium polysulfide (which treated to recover elemental sulfur) by an air stream and treating the ammonium polysulfide containing stream to recover elemental sulfur.

Asai et al. (1989) studied the rates of simultaneous absorption of H_2S and ammonia into water with a flat interface in an agitated vessel.

Rumpf et al. (1999) studied the simultaneous solubility of ammonia and hydrogen sulfide in water at temperature ranges from 313 to 393 K and pressures up to 0.7 MPa.

Lot of research works are also devoted to the study on the equilibrium solubility of pure H_2S, mixture of acid gases (H_2S and CO_2), and the mathematical representation of the experimental solubility data for H_2S, CO_2 and their mixture using various alkanolamines.

2.2 Reduction of Nitroarenes

Rode et al. (1999) defines the method to prepare *p*-aminophenol in a single-step catalytic hydrogenation of nitrobenzene (acid medium) whereas a conventional method of production of *p*-aminophenol is a two-step method involving iron-acid reduction of *p*-nitrophenol.

Jiang et al. (2001) Aqueous/organic two-phase CO selective reduction of nitroarenes catalyzed by the thermoregulated phase-transfer catalyst $Ru_3(CO)_9$(PEO-DPPSA)$_3$ (PEO-DPPSA-poly(ethylene oxide)-substituted 4 (diphenylphosphino)benzenesulfonamide) was inspected. The reduction proceed with good activity and selectivity toward nitro group when halogen, carbonyl or cyano groups present in the substrates.

Yadav et al. (2003) studied the reduction of nitroanisoles and other substituted nitroaromatics to the corresponding amines can be affected by aqueous inorganic sulfides, polysulfides and the rates of these biphasic reductions are responsive to intensification under phase transfer catalysis (PTC).

Xiaozhi Liu, Shiwei Lu(2003) investigated an efficient method for the production of aromatic amines by catalytic reduction of aromatic nitro compounds. They used selenium as a catalyst, where they found out that the aromatic nitro compounds are quantitively reduced by CO/H_2O to form the corresponding amines under atmospheric pressure. The reduction reactions occurs in high selectivity regardless of other reducible functionalities present on the aromatic ring. Phase transfer process of the catalyst (selenium) in the reaction is exists.

Yadav et al. (2004) studied the selective reduction of nitroaromatics to the corresponding amines. Nitroaromatics first dissolved in organic solvents and reduced using aqueous sodium sulfide and the phase transfer catalyst (TBAB) by selecting appropriate concentrations which resulted in three immiscible liquid phases. They also Compared L-L PTC to the L-L-L PTC which gives much higher rates of reaction and better selectivity.

Maity et al.(2006) studied the reduction of all the isomers of nitrotoluenes using aqueous ammonium sulfide as the reducing agent was carried out in an organic solvent medium toluene. The reactions were carried out under liquid–liquid mode with a PTC, tetrabutylammonium bromide (TBAB). The reaction rate for m-nitrotoluene was highest among the three nitrotoluenes, followed by p- and o-nitrotoluene.

Maity et al. (2007) studied the reduction of nitrochlorobenzenes (NCBs) carried out in an organic solvent (toluene) uisng liquid–liquid mode with phase transfer catalyst, TBAB.

Yadav at al.(2009) studied the synthesis of nitrophen using PEG-400 as a phase transfer catalyst in a solid-liquid (S-L) system from potassium 2,4-nitrophenolate and *p*-nitrochlorobenzene using xylene as a solvent under microwave irradiation. They also confirmed that the synergism of microwave activation and Solid-Liquid PTC using PEG 400 as a catalyst and solvent results in enhancements in the rate of reaction and selectivity of nitrophen.

Farhadi et al.(2010) prepared NiO nanoparticles by the thermal decomposition of bis(dimethylglyoximato) nickel(II) complex, a novel reusable heterogeneous catalyst for fast and efficient microwave-assisted reduction of nitroarenes with ethanol.

Robert Kaplanek, Viktor Krchnak(2013) reported the conditions for the fast and effective reduction of aromatic nitro compounds bound to hydrophobic polystyrene-based Wang and Ring resins. It utilize sodium dithionite in dichloromethane–water under PTC conditions. for this, Tetrabutylammonium hydrogen sulfate (TBAHS) was found to be an effective phase transfer catalyst and the method allows for the reduction of nitro groups to amino groups under mild conditions with 100% conversion. This is a superior alternative method to tin (II) chloride-based reduction.

Kiasat, Ali Reza (2011) gives the simple, practical and eco-friendly reduction of nitroarenes in which Polyethylene glycol was easily grafted to silica gel and used as a solid–liquid phase transfer catalyst in the reduction reaction. This silica-grafted polyethylene glycol is proved to be an efficient heterogeneous catalyst in the reduction of nitroarenes to the corresponding aromatic amines with zinc powder in water. The reduction reactions proceeded efficiently with excellent chemoselectivity without affecting other sensitive functional groups

There are various methods also employed for the reduction of nitroarenes as:

Bechamp reduction: It is the oldest industrially practiced method which involves the use of stoichiometric amounts of finely divided iron metal (also, tin, zinc, and aluminium can be employed) and water in the presence of small amount of acid. The formation of iron sludge is the key disadvantage of this process which is difficult to filter and dispose off in an environment. Additionally, this method neither used for the reduction of a single nitro group in a polynitro compound, nor used on substrates harmed by acid media (e.g., some ethers and thioethers).

Catalytic hydrogenation: It requires expensive equipment and facility to handle the hydrogen. In this method many problems arise due to the preparation of catalyst, poisoning hazards due to catalyst, and the risk of reducing other groups too. Metal hydrides like lithium aluminum hydride generally convert nitro compounds to a mixture of azoxy and azo compounds, besides being expensive. In this work, the sulfide reduction is employed and it enables chemoselective reduction of nitro compounds in the presence of C=C, azo and other nitro compounds. The sulfide reduction of nitroarenes is commonly carried out by sodium sulfide, disulfide, hydrosulfide, and ammonium sulfide.

2.3 Preparation of Aryl Amines Using Sodium Sulfide/Disulfide as Reducing Agent

Hojo et al. (1960) studied the kinetics of the reduction of nitrobenzene to aniline by using sodium disulfide in the form of methanolic solution. The rate of reaction was found to be proportional to the concentration of nitrobenzene and to the square of the concentration of sodium disulfide.

Bhave and Sharma (1981) studied the kinetics of two-phase reduction of three aromatic nitro compounds *m*-chloronitrobenzene, *m*-dinitrobenzene and *p*-nitroaniline by aqueous solutions of sodium monosulfide and sodium disulfide. The first order reaction rate with respect to the concentration of nitroaromatics and sulfide was found out.

Pradhan and Sharma (1992b) reduced chloronitrobenzenes to the corresponding chloroanilines with sodium sulfide in the presence and absence of a Phase Transfer Catalyst. In the solid-liquid mode, the reactions of *o*-chloronitrobenzene and *p*-chloronitrobenzene gave 100% chloroanilines in the absence of a catalyst and 100% dinitrodiphenyl sulfides in the presence of a catalyst. The reaction of *m*-chloronitrobenzene with solid sulfide, gave *m*-chloroaniline as the only product even in the presence of a catalyst. In the liquid-liquid mode, all three substrates gave amine as the only product in the presence and absence of a catalyst.

Pradhan (2000) reduced the nitrotoluenes (*o*-, *m*-, and *p*-) to the corresponding toluidines using sodium sulfide in the liquid-liquid and solid-liquid modes by TBAB as a Phase Transfer Catalyst. In the liquid-liquid mode reactions of all the three nitrotoluenes were found to be kinetically controlled. In solid-liquid mode, the reactions of *o*- and *p*-nitrotoluenes were kinetically controlled and *m*-nitrotoluene was found to be mass transfer controlled.

Yadav et al. (2003a) studied the kinetics and mechanisms of liquid–liquid Phase Transfer Catalytic reduction of *p*-nitroanisole to *p*-anisidine. The detailed kinetics and mechanisms of complex liquid–liquid Phase Transfer Catalytic processes was reported. The reaction rate was proportional to the concentration of TBAB (catalyst), *p*-nitroanisole(reactant) and sodium sulfide.

Yadav et al. (2003b) investigated the reduction of *p*-chloronitrobenzene with sodium sulphide under different forms of phase transfer catalysis, such as liquid-liquid, liquid-solid, and liquid-liquid-liquid processes.

2.4 Preparation of Aryl amines Using Ammonium Sulfide

There are reports for the preparation of aryl amines using three different types of ammonium sulfide as: (a) aqueous ammonium sulfide, (b) alcoholic ammonium sulfide, and (c) ammonium sulfide. They prepared from an equivalent amounts of ammonium chloride and crystalline sodium sulfide dissolved in ammonium hydroxide or alcohol.

Cline and Reid (1927) reduced 2,4-dinitroethylbenzene by alcoholic ammonium sulfide. A mixture of 50gm of 2,4-dinitroethylbenzene in 150gm of ethyl alcohol was treated with 150gm of concentrated aqueous ammonia. The mixture then saturated with H_2S and boiled until a gain in weight of 30gm was affected. This solution was poured into ice and the amine separated out. It was filtered off and dissolved in dilute HCl. The acid solution was boiled with animal charcoal, filtered and allowed to cool. The hydrochloride separating out was purified by recrystallization several times from dilute acid, using animal charcoal each time. The base was set free by NH_3 and recrystallized from dilute alcohol, which melts at 45^oC.

Lucas and Scudder (1928) reduced 2-bromo-4-nitrotoluene to 2-bromo-4-aminotoluene in an alcoholic solution of ammonium sulfide.

Murray and Waters (1938) reduced *p*-nitrobenzoic acid by using ammonium sulfide which prepared by dissolving the equivalent amounts of ammonium chloride and crystalline sodium sulfide in ammonium hydroxide or alcohol.

Idoux and Plain (1972) studied the selective reduction of a series of 1-substituted 2,4 dinitrobenzenes by ammonium sulfide or sodium hydrosulfide. It was concluded that the reduction took place at the position to which electron donation is the least by 1- substituent.

Meindl et al. (1984) prepared 3-amino-5-nitrobenzyl alcohol from 3,5-dinitrobenzyl alcohol using the solution of ammonium sulfide prepared by adding a solution of $Na_2S.9H_20$ (96gm, 0.4 mol) in 250 ml of MeOH to a solution of NH_4Cl (85.6gm, 1.6 mol) in 250 ml of MeOH and separating the NaC1. This solution was added within 30 min to a solution of 3,5-dinitrobenzyl alcohol (39.6gm, 0.2 mol) in 700 ml of boiling MeOH, and the mixture refluxed for 5 hrs. After the mixture was cooled to room temperature, the resulting precipitate of sulfur was removed. HCl (2N) was added and the solvent was distilled off. After the removal of starting material with ether, the aqueous solution was alkalized and the product extracted with ether: yield 62%; M.P. 91.5 ^oC.

There are some recent reports on reduction of nitrotoluene (Maity et al. 2006a and 2006b) and nitrochlorobenzenes (Maity et al., 2008a) by aqueous ammonium sulfide using TBAB as

catalyst. Maity et al. (2008b) has also performed reduction of pnitrotoluene by aqueous ammonium sulfide using anion-exchange resin as catalyst. Also there are report of reduction of nitrotoluene by aqueous ethanolamine (Maity et al., 2006) and that of o-anisole by H_2S-rich diethanolamine (Maity, 2007), both in presence of TBAB catalyst. But there is no report of reduction of chloronitrobenzene by H_2S-rich monoethanolamine.

CHAPTER 3

EXPERIMENTAL

3. Experimental

3.1 Chemicals

Toluene (≥ 99%) and liquor ammonia (~ 26%) of analytical grade were bought from Merck (India) Ltd., Mumbai, India. Amberlite IR 400 was also obtained from Merck (India) Ltd., Mumbai, India. Monoethanolamine (≥98%) of synthesis grade was procured from Merck (India) Ltd., Mumbai, India. m-chloronitrobenzene was purchased from Sigma-Aldrich Corporation Bangalore, India.

3.2 Equipment

All the reactions were carried out in batch mode in a fully baffled mechanically agitated glass reactor of capacity 250 cm^3. 2cm diameter six-bladed glass disk turbine impeller with the provision of speed maintenance, located at an approximate height of 1.5 cm from the bottom of the reactor, was used for stirring the reaction mixture. The reactor assembly was kept in a constant temperature water bath whose temperature could be controlled within ±1^oC. The schematic diagram of the experimental setup is as shown in Fig. 3.1.

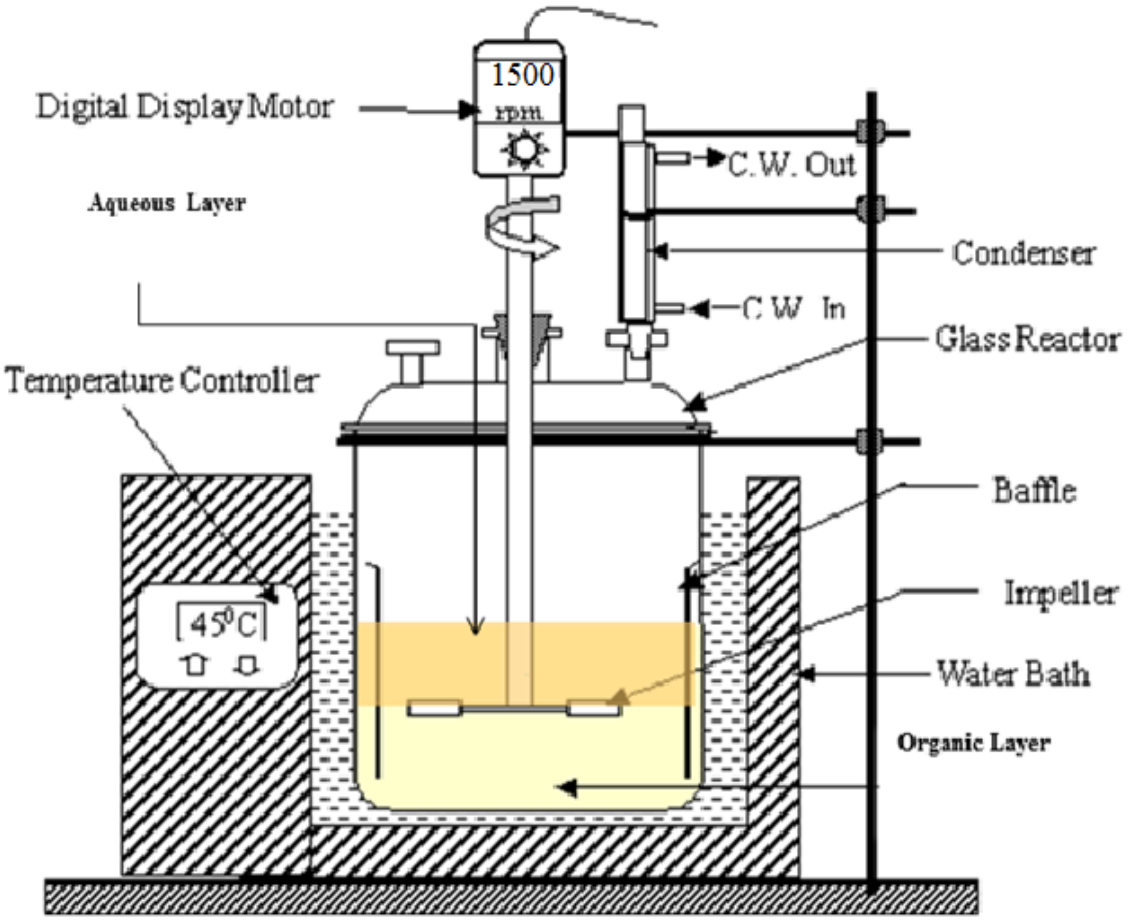


Fig. 3.1: Schematic of the batch reactor assembly

3.3 Preparation of H_2S-Rich Aqueous Alkanolamines

For the preparation of H_2S-rich aqueous monoethanolamine (MEA), around 30-35wt% aqueous alkanolamine solution was prepared first by adding a suitable quantity of desired alkanolamine in distilled water. Then H_2S gas was bubbled through this aqueous ammonium sulfide or aqueous alkanolamines in a 500cm^3 standard gas bubbler. The H_2S gas is generated using Kipp's apparatus in which ferrous sticks come into the contact with 1M sulfuric acid solution. Since the reaction of H_2S with ammonium hydroxide and with alkanolamines is exothermic, the gas bubbler containing ammonium hydroxide and aqueous alkanolamine was kept immersed in an ice water bath in order to prevent the oxidation of sulfide and thus to prevent the formation of disulfide. After the approximate 5-6 hrs of operation Liquid samples were withdrawn and analyzed for sulfide content (Scott, 1966). The gas bubbling was continued until the desired sulfide concentration was obtained in the aqueous ammonia or alkanolamines.

3.4 Experimental Methodology

Two approaches were tried while performing experiments. One is conventional One-Variable-at-a-Time (OVAT) approach (or a single variable approach) where reactions were performed by changing one variable at a time and keeping all other variables fixed. The second one is Design of Experiment (DoE) where effect of simultaneous change in two parameters on reaction outcome (conversion, selectivity) is considered.

3.4.1 One-Variable-At-A-Time (OVAT) approach

As in most scientific disciplines, chemists have historically followed the practice of changing one variable at a time (OVAT) during optimization (Akhnazarova and Kafarov, 1982; Box et al., 1978). This method is useful to see the main effect of each variable on conversion and selectivity separately. The data obtained by this method, can be used to get the order of reaction, optimize a simple reaction system, estimate kinetic parameters, to evaluate some thermodynamic parameters. For a complex system, the conventional OVAT approach is time-consuming, non-feasible and inept of getting the true optimum condition due to the lack of interactions among the variables. Also, for systems where mechanism of reaction is not well known, this approach is inadequate for model building and optimization.

3.4.2 Design of Experiment (DoE)

An alternative approach to OVAT is Design of Experiment. In the DoE approach, process variables are first 'screened' to determine which are important to the outcome. To get 'optimization' best settings for the important variables are determined. In particular, factorial designs and response surface methodologies (RSM) have been successfully applied as DoE techniques in both discovery and development. RSM is a statistical technique for developing and optimizing processes, its response (sometimes called objective function) is influenced by several variables (Khuri and Cornell, 1987; Montgomery, 2001; Myres and Montgomery, 2002). RSM is a combination of mathematical and statistical procedures. It is applied to study relationships between independent variables and response. Multivariate equations can be solved by using quantitative data obtained from accurately designed experiments. Response surfaces are the graphical representations of these equations. These surfaces actually explain individual, cumulative, and interactive effects of test variables on response. Further, it determines optimal

factorial combination of variables that results in maximum response (Khuri and Cornell, 1987; Montgomery, 2001). RSM is widely used now-a-days for process optimization through a relatively smaller number of systematic experiments that can reduce time, cost and resources. It has the advantage that it allows the user to gather large amounts of information from a small number of experiments. Another advantage of any DoE methods is that it doesn't require any knowledge of detailed mechanism of the reaction system and it just requires the input variables and the responses. In the RSM, the effects of individual variables and their interactions on the response can be observed. Since 1990s, there are many examples of parallel synthesis and DoE methods have been applied for process optimization. However, RSM has been used so far as a tool mostly for optimization in biomedical, biochemical, agricultural and pharmaceutical fields with very few applications in chemical fields.

One of the mostly used RSM method is Central Composite Rotatable Design (CCRD) method. In this method, selection of variables was carried out on the basis of results obtained in the preliminary study, considering limits for the experimental set-up, working conditions for each chemical species and the previous experiences in dealing with variables to get desired results. For statistical calculations, the variables *Xi* were coded as *xi* according to the following relationship,

$$xi = \frac{Xi - Xo}{\partial X}$$

Where, *xi* is dimensionless value of independent variable,

Xi represents the real value of independent variables,

X_0 is value of the *Xi* at the centre point and

∂X represents the step change.

The CCRD helps in investigating linear, quadratic, cubic, and cross-product effects of reaction variables on responses. The CCRD permits the response surface to be modeled by fitting a polynomial with the number of experiments equal to $2f + 2f + n$, where f and n are the number of factors and centre runs respectively. The center points were used to evaluate the experimental error and the reproducibility of the data. The axial points ($2f$) are chosen such that they allow rotatability, which ensures that the variance of the model prediction is constant at all points

equidistant from the design center. Replicates of the test at the center are very important as they provide an independent estimate of the experimental error.

3.5 Experimental Procedure

In this experimental run, 50cm^3 of aqueous phase containing a known concentration of sulfide was taken into the reactor and kept well agitated until the steady state temperature was reached. Then 50$cm^3$of the organic phase containing measured amount of organic reactant (m-chloronitrobenzene), catalyst (Amberlite IR 400) and solvent (toluene) was added into the reactor. The reaction mixture was then agitated at a constant speed of stirring. About 0.5cm^3 of sample from the organic phase was withdrawn at a regular time interval after stopping the agitation and allowing the phases to separate.

3.6 Analysis

3.6.1 Determination of Sulfide Concentration

Iodometric test was used to determine initial sulfide concentrations which is explained in brief below (Scott, 1966).

Preparation of standard (0.025 M) KIO_3 solution: 4.28gm of KIO_3 was weighed accurately and dissolved in distilled water and was made up to 1 L in a graduated volumetric flask.

Preparation of standard (0.1 M) sodium thiosulfate solution: 25gm of $Na_2S_2O_3.5H_2O$ crystals was weighed and dissolved in distilled water and made up to 1 L in a graduated volumetric flask with distilled water. About 0.1g of sodium carbonate or three drops of chloroform was added to the solution to keep it for more than a few days.

Standardization of sodium thiosulfate solution by standard potassium iodate solution: 25 cm^3 of 0.025M KIO_3 solution was taken and 1g (excess) of potassium iodide (KI) was added to it followed by 3 cm^3 of 1M sulfuric acid. The liberated iodine (I_2) was titrated with thiosulfate solution. When the color of the solution became a pale yellow, it was diluted to 200 cm^3 with distilled water. 2 cm^3 of starch solution was added, and the titration was continued until the color changed from blue to colorless. The chemical reaction involved in this titration is given below.

$$KIO_3 + 5KI + 3H_2SO_4 \rightarrow 3I_2 + 3H_2O + 3K_2SO_4$$

$$2\ Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Therefore, 1 mole of $KIO_3 \equiv 3 \times 2$ mole of $Na_2S_2O_3$

$$\text{strenght of thiosulfate solution} = \frac{6 \times \text{strenght of KI}O_3 \times \text{volume of KI}O_3}{\text{volume of sodium thiosulfate}}$$

Estimation of sulfide concentration: Hydrogen sulfide and soluble sulfides can be determined by oxidation with potassium iodate in an alkaline medium. $15cm^3$ of standard (0.025M) potassium iodate solution was taken in a conical flask. $10cm^3$ of sulfide solution containing about 2.5 mg of sulfide was then added to it followed by the addition $10cm^3$ of 10M sodium hydroxide solution. The mixture was boiled gently for about 10 minutes, cooled with the tap water, fridge and $5cm^3$ of KI solution and 20cm3 of 4M sulfuric acid solution were added to it. The iodine was liberated which is then titrated. The liberated iodine is equivalent to the unused potassium iodate, with a standard 0.1M sodium thiosulfate in the usual manner. The potassium iodate in the alkaline medium oxidizes the sulfide to sulfate as shown in the following reaction. For sulfide solution having sufficiently high sulfide concentration, suitable dilution was made before the estimation of sulfide as mentioned in the above procedure.

$$4IO_3^- + 6OH^- + 3S_2\text{-} \rightarrow 3SO_4^{2-} + 4I^- + 6H_2O$$

4 mole of $IO_3\text{-} \equiv 3$ mole of S^{2-}

$$\text{H2S concentration} = [15 \times \text{S(iodate)} - \frac{\text{V(thiosulfate)} \times \text{S(thiosulfate)}}{6}] \times \frac{3}{4} \times \frac{\text{Nd}}{10}$$

Where, S(iodate) = Strength of KIO_3

V(thiosulfate) = volume of thiosulfate

S(thiosulfate)= strength of thiosulfate

3.6.2 Analysis of Organic Phase

Samples were analyzed by gas liquid chromatography (GLC). GC-7890B, DB-5MS, 2m* 3mm capillary column, FID detector was used with nitrogen as the carrier gas during the analysis Chromatopac Data Processor was used for the analysis.

CHAPTER 4

RESULT AND DISCUSSION

(PARAMETRIC STUDY)

4. Result and Discussion

(Parametric Study)

4.1 Effect of stirring speed

To define the influence of external mass transfer resistance for the transfer of the reactants to the reaction phase, the effect of stirring speed on the rate of reaction of m-CNB was studied in the range 1000-2000 RPM. However other experimental conditions was kept identical. The conversion of m-CNB in the presence of PTC (Amberlite IR 400) as shown in Fig. 4.1. To increase the mass transfer rate the reactions systems need a relatively larger interfacial area. However, the active intermediate of the catalyst (Q_2S), is hydrophobic in nature and likes to stay in the organic phase, in which the interfacial area is not so important.

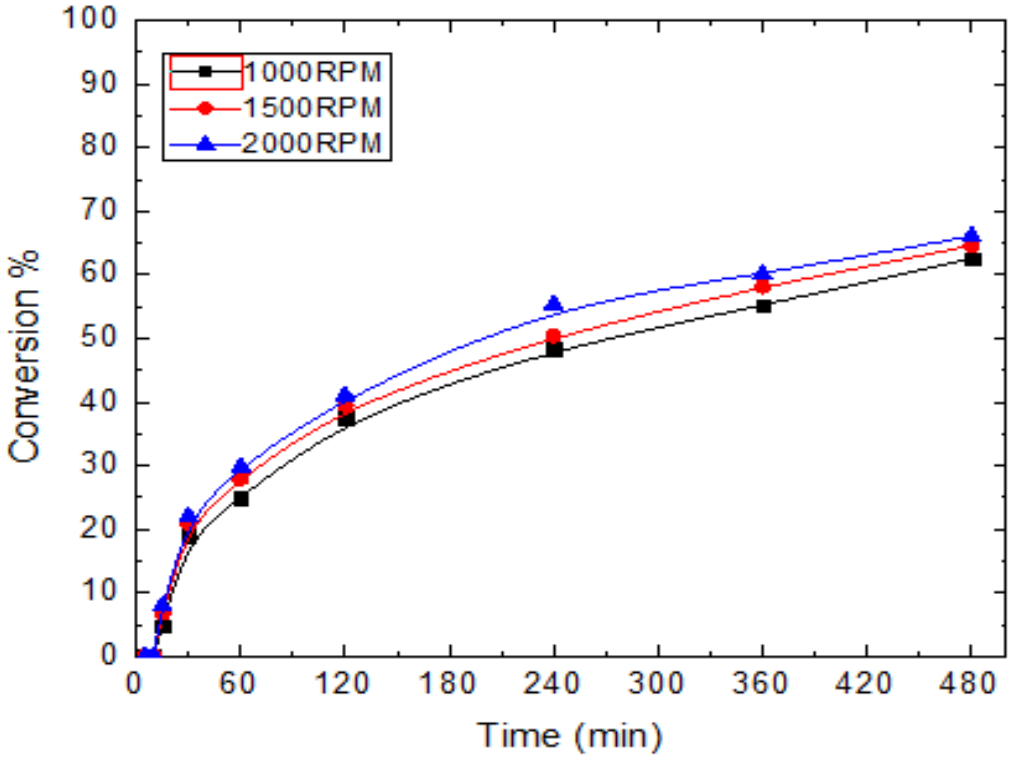


Fig.4.1: Effect of stirring speed on the conversion of m-CNB.

Operating conditions: Volume of organic phase =50 ml; concentration of m-CNB = 1.27M org. phase; concentration of toluene = 8.17M org. phase; volume of aqueous phase = 50 ml, concentration of catalyst = 0.58 M org. phase; concentration of sulfide = 2.53 M, MEA/H_2S mole ratio =2.287; temperature = 333 K.

Reactions may be considered as kinetically controlled for all practical purposes as there is mass transfer factors become unimportant because of very small variation of the reaction rate with the stirring speed. Hence, all the other experiments were performed at a stirring speed of 1500 RPM in order to eliminate any mass transfer resistance.

4.2 Effect of temperature

The present work examines the reaction of m-CNB with Toluene catalyzed by a resin catalyst Amberlite IR 400 in the presence of H_2S-rich aqueous MEA under various reaction temperatures was studied under otherwise similar reaction conditions. The temperatures are varied in the range of 30–60^oC. Fig.4.2 (a) shows the effect of temperature on conversion of m-chloronitrobenzene. As predictable, as per the transition state theory the rates of most organic reactions increase with the increase in temperature. For this reason, it is considered that increasing temperature is likely to endorse slow organic phase reactions in PTC system. It is obvious that the reactivity (conversion) of m-CNB is increased with an increase in the temperature. This has a reason that the number of reactant molecules, which possess larger activated energy at a higher temperature. Thus the conversion of m-CNB is increased. On the other hand collision of the reactants at higher temperature is also increased which increases the reaction rate with increasing temperature.

Arrhenius plots of *ln* (initial rate) vs. 1/T were made for all m-CNB (Fig. 4.2(b)). The apparent activation energies for the kinetically controlled reaction were calculated from the slopes of the straight line as 56.16 KJ/mol. The high values of apparent activation energies again confirm that the reaction systems are kinetically controlled.

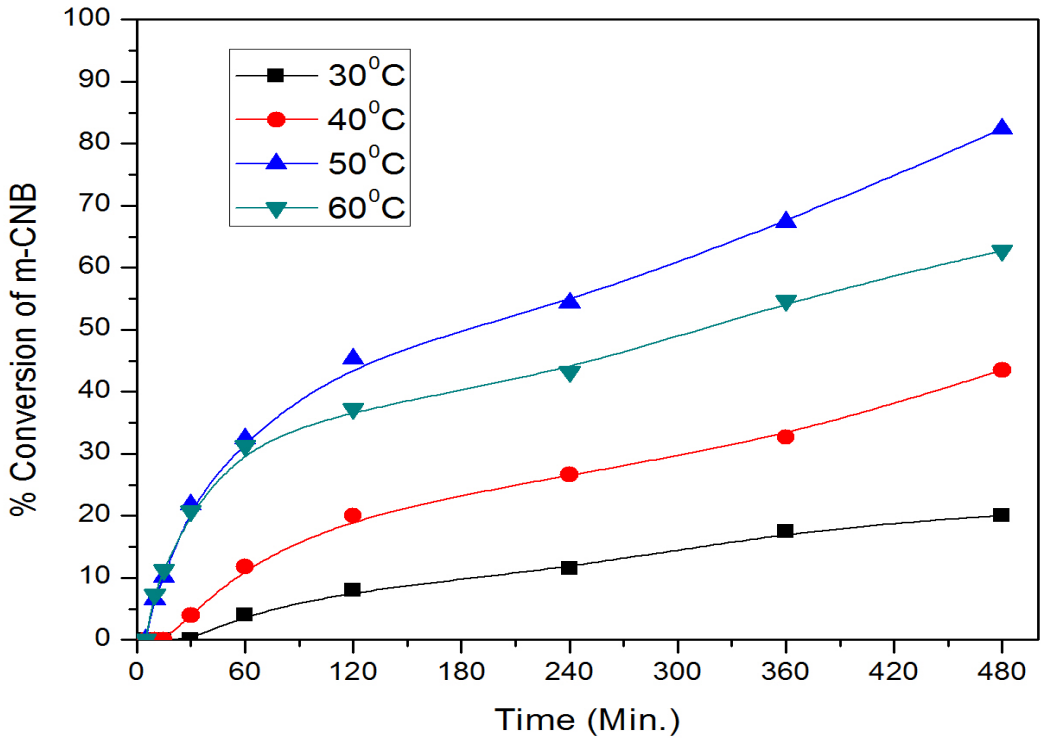


Fig.4.2 (a): Effect of Temperature

Operating Conditions: Volume of organic phase =50ml, Volume of Aqueous Phase =50ml, Concentration of m-CNB =1.27M org. phase, concentration of toluene 8.17M org. phase, concentration of catalyst = 0.58M org. phase, Sulfide concentration = 2.53M, MEA/H_2S ratio = 2.287, Stirring speed = 1500 rpm.

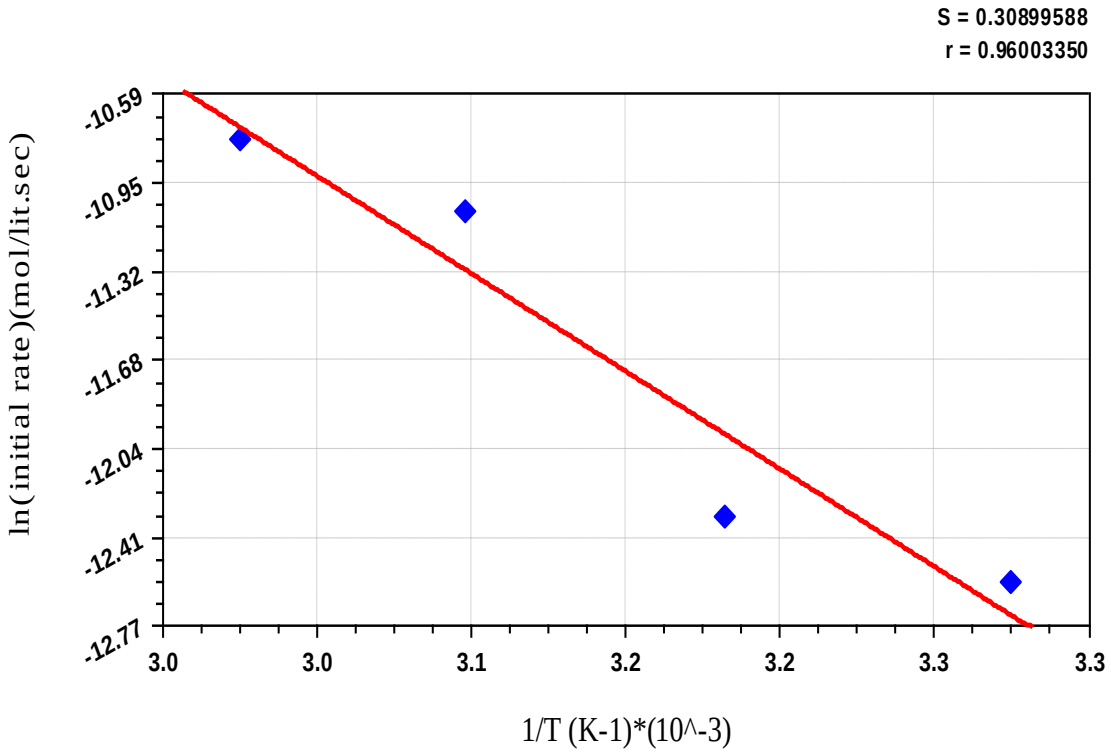


Fig.4.2 (b): Arrehenius Plot of ln(initial rate) vs. 1/T

4.3 Effect of Catalyst (Amberlite IR 400) quantity:

For kinetically controlled reduction of m-CNB by aqueous MEA, The effect of catalyst (Amberlite IR 400) concentration on the conversion of m-CNB was studied in the range of 0 – 0.58M org. phase. As the catalyst load increases, the conversion of m-CNB as well as the reaction rate increases. Only by increasing the catalyst concentration, reactant conversion of more than 60% was achieved whereas it was about 32% without catalyst even after 8hrs. of reaction under otherwise identical conditions.

For liquid-liquid-solid tri-phase reactions, the overall rate of reaction is given by rate of transference of anions from aqueous phase to organic phase. In presence of PTC, the transportation of anions (in present case S^{2-} and HS^{-}) is facilitated and the reaction becomes organic-phase limited. The hydrosulfide (HS^{-}) and sulfide (S^{2-}) ions present in the aqueous phase readily form ion pairs [$Q^{+}HS^{-}$ and $Q^{+}S^{2-}Q^{+}$], with quaternary cations, [Q^{+}] and are transferred to the organic

phase and then reacts with benzyl chloride. With increased catalyst concentration, more amount of $[Q^+]_2S^{2-}$ ion pair is formed and transferred to the organic phase and reacts with m-CNB to form m-CA.

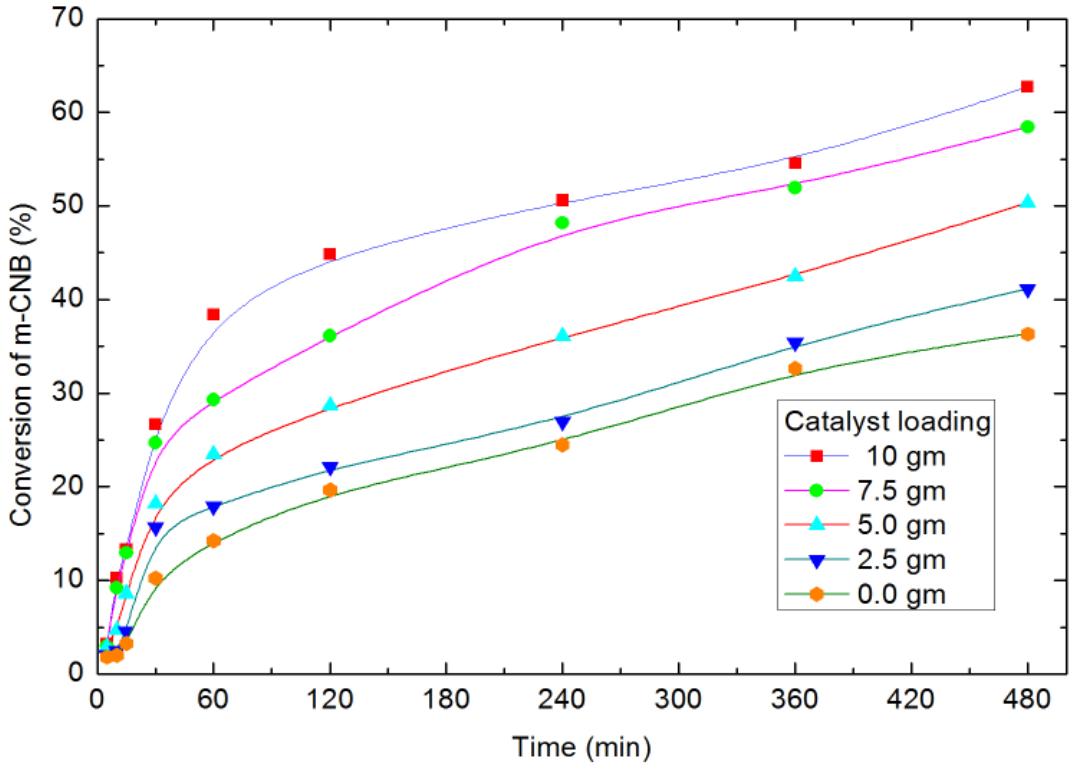


Fig.4.3 (a): Effect of Catalyst (Amberlite IR 400)

Operating Conditions: Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, Concentration of m-CNB –1.27M org. phase, concentration of toluene= 8.17M org. phase, concentration of catalyst=0-0.58M org. phase, Sulfide concentration – 2.53M, MEA/H2S ratio – 2.287, Stirring speed – 1500 rpm, Temperature 323K.

To determine the order of reaction with respect to Amberlite IR 400 (catalyst) concentration, the initial reaction rate was calculated at different Amberlite IR 400 concentrations. plot of *ln* (initial rate) against *ln* (Amberlite IR 400 concentration) was made and shown in Fig. 4.3(b). From the slope of the linear fit line, the order of reaction was determined. The slope of the line is found out to be 0.88 which is close to unity.

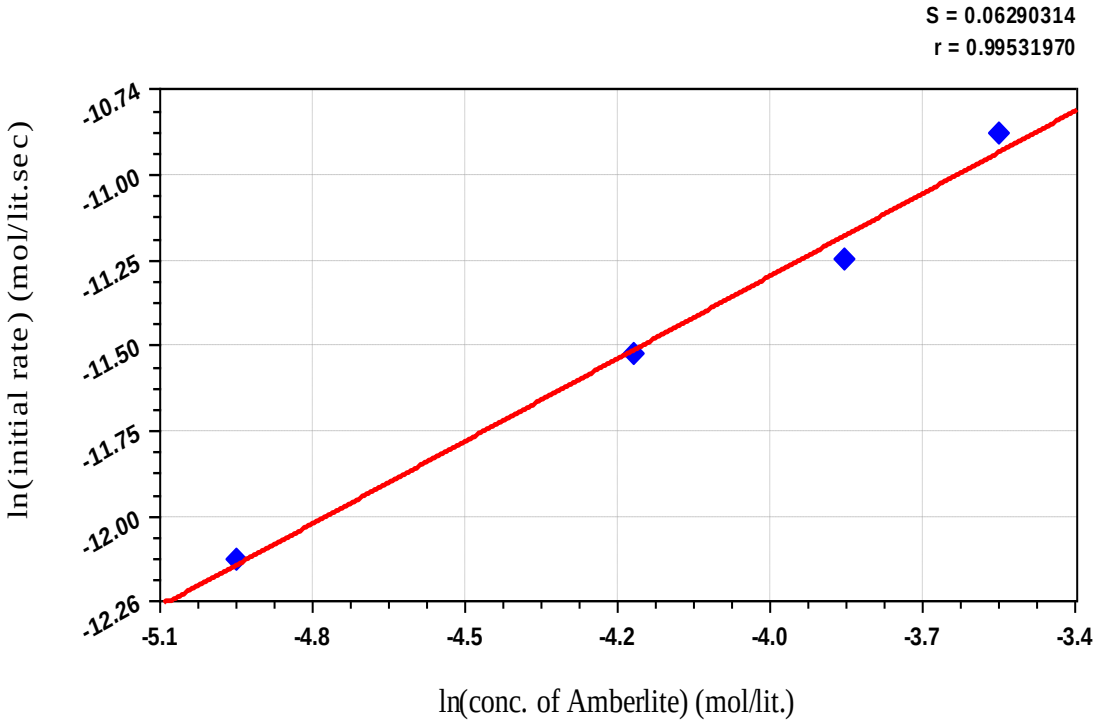


Fig.4.3(b) ln(initial rate) vs ln(Amberlite IR 400 concentration)

4.4 Effect of *m*-chloronitrobenzene concentration

The effect of concentration of m-CNB on its conversion was studied in the presence of Amberlite IR 400 under otherwise identical experimental conditions, as shown in Fig. 4.4(a). As the concentration of m-CNB increased, the conversion of m-CNB was decreased.

As expected, the increase in the reaction rate during the initial stage of reaction is due to the increase in the concentration of m-CNB. Since the amount of sulfide in the aqueous phase remained the same for all the experimental runs, the conversion of m-CNB dropped beyond a certain concentration as shown in Fig. 4.4(a). Conversion and reaction rate were found to increase with decrease in m-CNB concentration at the end of 8 hours of reaction time.

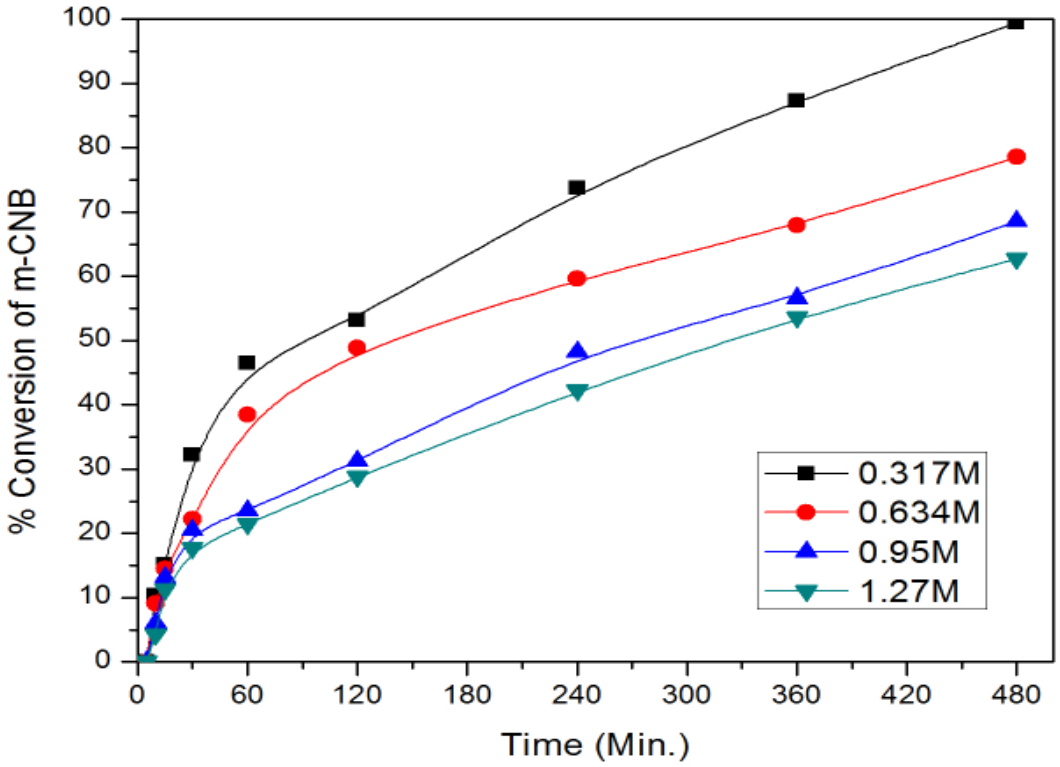


Fig.4.4 (a): Effect of Reactant concentration

Operating Conditions: Volume of organic phase – 50ml, Volume of Aqueous Phase – 50ml, concentration of toluene= 8.17M org. phase, concentration of catalyst=0.58M org. phase, Sulfide concentration – 2.53M, MEA/H2S ratio – 2.287, Stirring speed – 1500 rpm, Temperature- 333K.

From the plot of *ln* (initial rate) vs. *ln* (initial m-CNB concentration), (Fig. 4.4(b)) the order of reaction with respect to m-CNB concentration was obtained as 0.95, which is close to unity. Hence the reaction is first order with respect to the concentration of reactant.

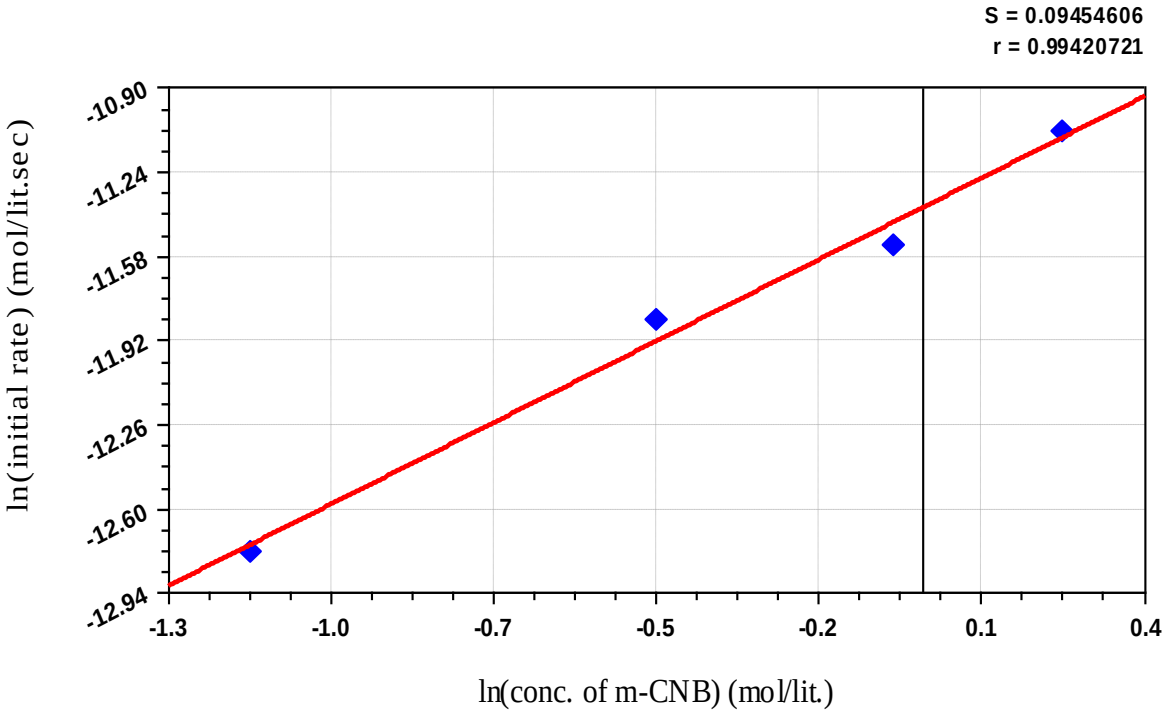


Fig.4.4 (b) Plot of ln(initial rate) vs. ln(reactant concentration)

4.5 Effect of initial sulfide concentration

Fig. 4.5(a) shows the effect of sulfide concentration in the aqueous phase on the conversion of m-CNB. With an increase in the concentration of sulfide, the conversion of m-CNB and the reaction rate increases. Sulfide concentration was varied in the range of 1.5 to 2.53M.

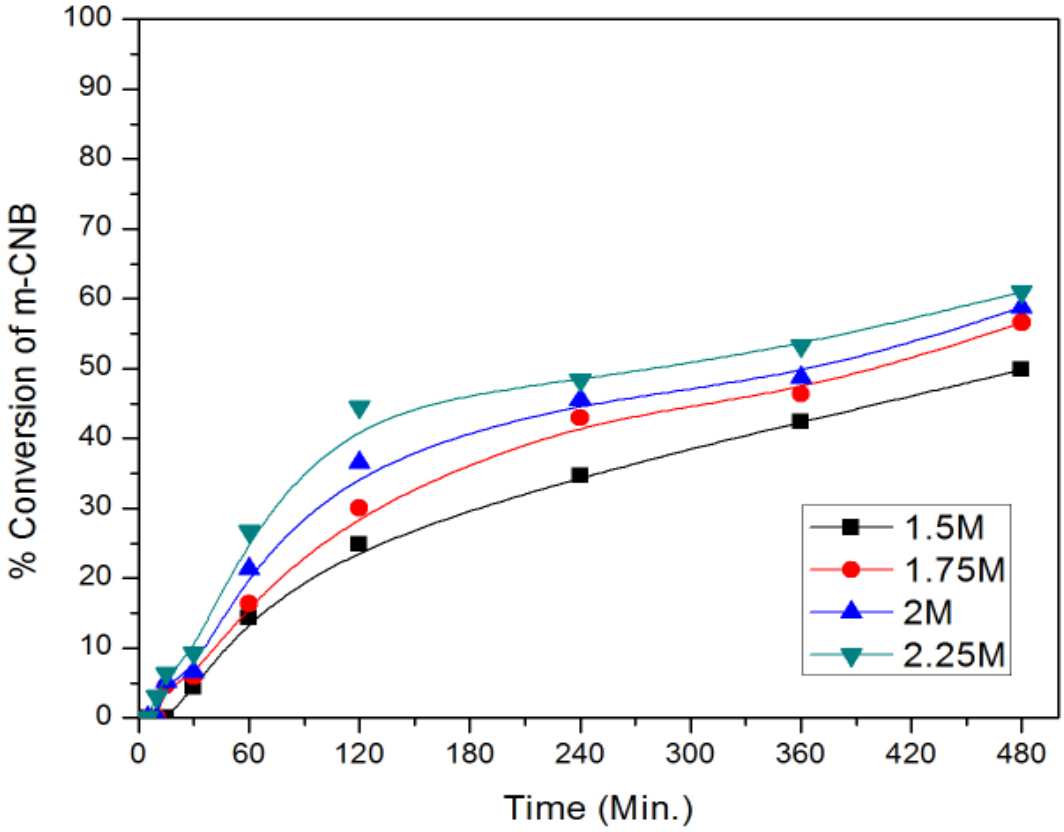


Fig.4.5 (a): Effect of Sulfide Concentration

Operating Conditions: Volume of organic phase= 50ml, Volume of Aqueous Phase=50ml, Concentration of m-CNB=1.27M org. phase, concentration of toluene= 8.17M org. phase, concentration of catalyst=0.58M org. phase, Sulfide concentration = 2.53M, MEA/H_2S ratio = 2.287, Stirring speed = 1500 rpm.

From the plot of *ln* (initial rate) against *ln* (initial sulfide concentration) (Fig. 4.5(b)), the slope of linear fit line was found out to be to be 1.58. Since this value is closer to 2, the reaction was considered 2^{nd}order with respect to the sulfide concentration. For the reduction of m-CNB with aqueous ammonium sulfide, the reaction rate was also reported to be 2^{nd} order with respect to sulfide concentration (Maity et al., 2008).

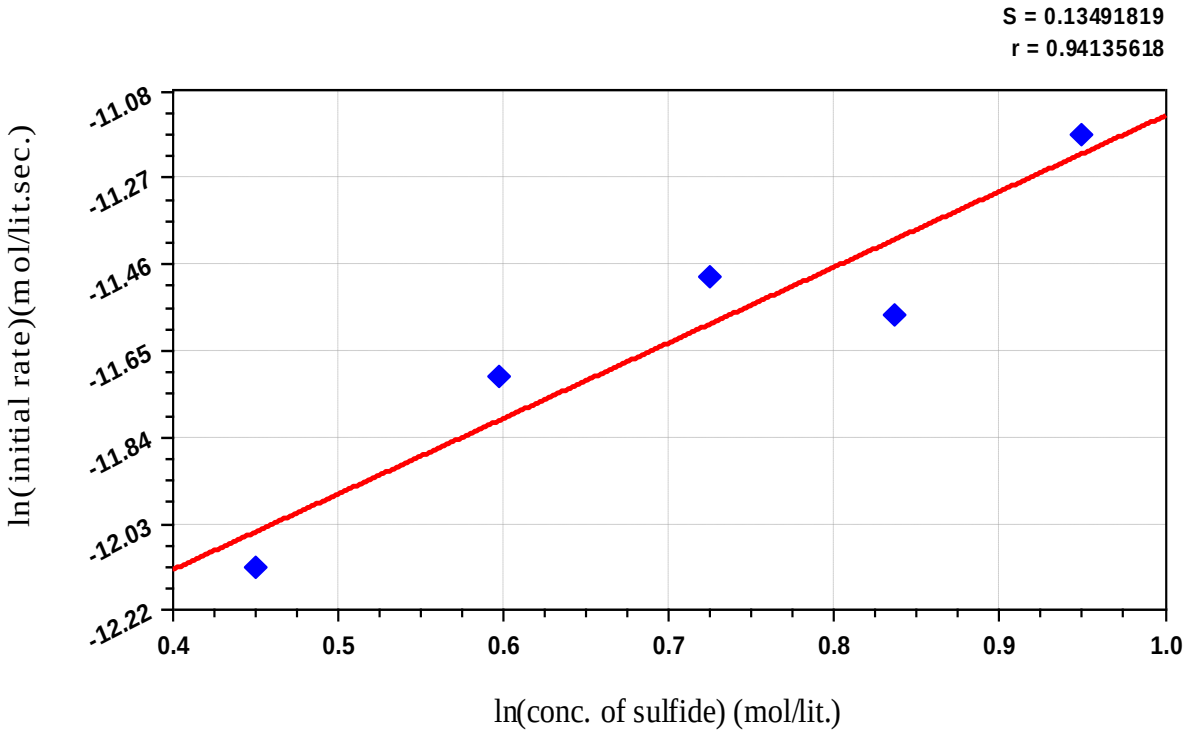


Fig. 4.5(b): Plot of ln(conc. Of sulfide) vs. ln(initial rate)

4.6 Effect of MEA concentration

Although MEA does not take part in the reaction with chloronitrobenzes, it affects the equilibrium among MEA, H_2S, and water. Because of this there was two active anions, sulfide (S^{2-}), and hydrosulfide in the aqueous phase. These two active anions participate in two different reactions with MEA. In the presence of a base MEA, the dissociation equilibrium shifts toward more ionization and the concentration of sulfide ions relative to hydrosulfide ions in the aqueous phase increases with an increase in MEA concentration. Hence, only by changing the MEA concentration with constant sulfide concentration in the aqueous phase, it would be easy to prove the existence of two different reactions.

MEA concentrations (keeping constant sulfide concentration) was prepared by taking 27cm^3 of H_2S-rich aqueous MEA (with known sulfide and MEA concentrations). Then adding various proportions of pure MEA and distilled water to it in such a way that the total volume was make up to 50 cm^3.

The effect of MEA concentration on the conversion of m-CNB is shown in Fig. 4.6. With an increase in the concentration of MEA, the conversion of m-CNB was found to decrease up to a

certain reaction time. Beyond that, the opposite trend was observed that is at higher MEA concentration, higher m-CNB conversion was achieved. The color of the aqueous solution changes from greenish yellow, at the start of reaction, then to orange and to reddish brown. The characteristic reddish brown color is due to the formation of polysulfide as reaction proceeds. The reddish brown color is useful in indicating the extinct of the chemical reaction.

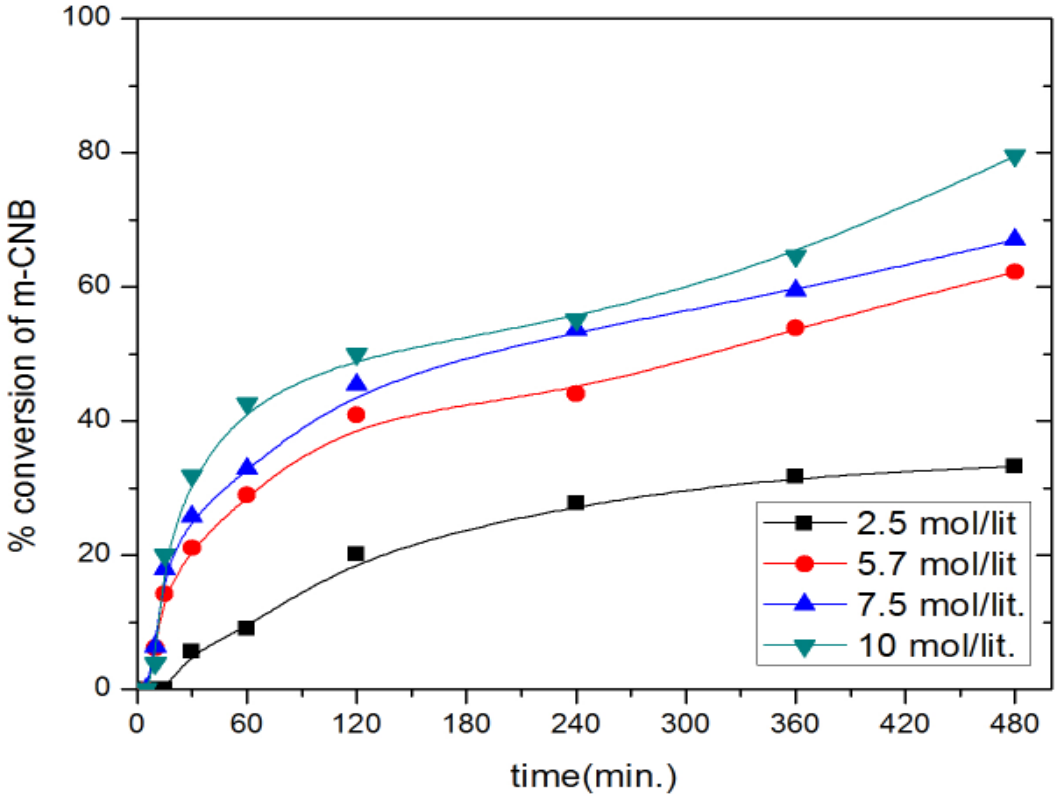


Fig.4.6: Effect of MEA Concentration

Operating Conditions: Volume of organic phase = 50ml, Volume of Aqueous Phase = 50ml, Concentration of m-CNB =1.27M org. phase, concentration of toluene= 8.17M org. phase, concentration of catalyst=0.58M org. phase, Sulfide concentration = 2.53M, Stirring speed = 1500 rpm.

4.7 Recycle and Reusability of Catalyst (Amberlite IR 400)

After the completion of the kinetic run, the agitation was stopped and the phases were allowed to separate in a separating funnel into three layers (L-L-S). When the phases were clearly

separated, the organic phase containing the product was removed. The reusability was found to be good up to four uses as shown in Fig.4.7.

After use the catalyst microsphere was filtered from the solution by the use of filter paper. It was washed with NaCl and water and was dried to remove the adsorbed substance. The catalyst obtained was reused and the data obtained is shown in fig.4.7.

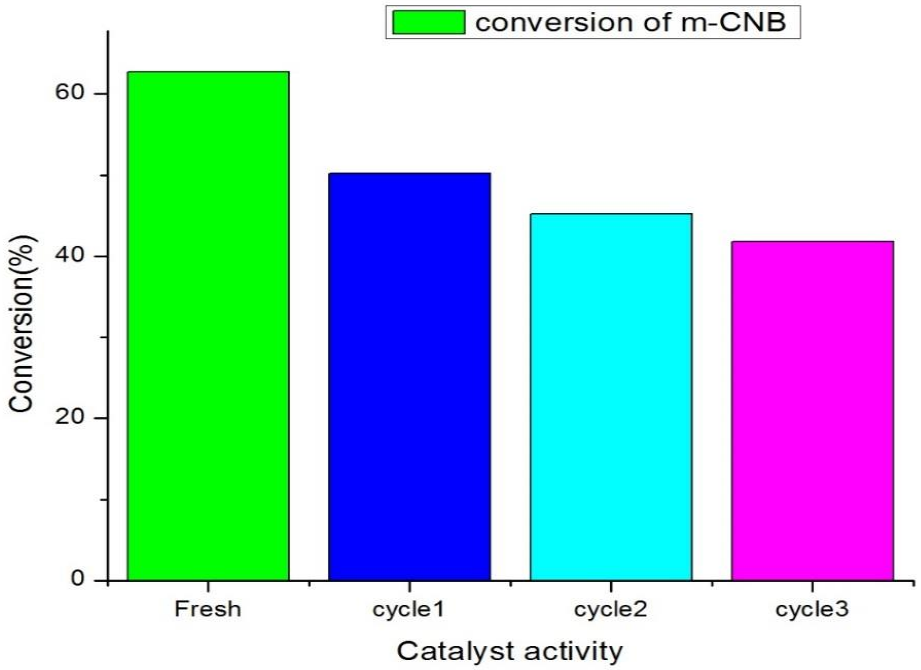


Fig. 4.7: Conversion of m-CNB with the cycle number.

It can be seen upto the 4 cycles, the activity of tri phase catalyst Amberlite IR 400 remains nearly unchanged. This tells that Amberlite has got excellent reuse property and high stability.

CHAPTER 5

CONCLUSIONS AND FUTURE SCOPE

5. Summary and Conclusions

The work carried out in this thesis has led to the development of a state-of-the art process to produce fine chemicals utilizing the H_2S present in various byproduct gas streams. In accordance with the present process, the H_2S present in the gas streams can be utilized to produce fine chemicals in two steps: (i) Removal of H_2S from gas stream by ammonia and alkanolamine-based processes (ii) Production of value-added fine chemicals using H_2S-rich solution obtained from the first step. Since the removal of H_2S by ammonium hydroxide or alkanolamines are well established and industrially practiced one, the present work deals with a detailed study for the production of fine chemicals using H_2S-rich aqueous ammonia or alkanolamine in the batch mode. The ammonia-based process is suitable for the gas streams containing both NH_3 and H_2S because both the impurities can be removed simultaneously in a single step, whereas alkanolamine-based process can be used for gas streams containing no ammonia because of its other advantages over the ammonia.

The reactions of nitroarenes with H_2S-rich aqueous alkanolamines were conducted batch-wise in presence of an organic solvent, toluene under liquid-liquid-solid mode with the phase transfer catalyst (PTC), Amberlite IR 400. The influence of various process variables (speed of agitation, catalyst loading, concentration of reactants, temperature, MEA concentration, elemental sulfur loading) on the reaction rate, conversion, and selectivity was studied. A suitable mechanism was proposed based on the effects of various parameters on the reaction rate and conversion to explain the course of the reaction. Estimation of kinetic parameters has been done either by development of an empirical kinetic model from experimental analysis.

The reduction of m-chloronitrobenzene (m-CNB) by H_2S-rich aqueous MEA was studied under liquid–liquid-solid mode in presence of a PTC (Amberlite IR 400). The selectivity of m-chloroanilines was found to be 100%. The reaction was found to be kinetically controlled with apparent activation energies of 56.16 KJ/mol. The overall rate of reduction of m-CNB was found to be proportional to the concentration of catalyst and m-CNB, and to the square of the concentration of sulfide.

In the reduction of m-CNB by H_2S-rich aqueous MEA, elemental sulfur was determined to be formed at a very high selectivity under certain experimental conditions. In this process, aryl amines together with elemental sulfur (the only product of the Claus and LO-CAT process) were

obtained. Moreover, the regeneration of the H_2S-rich solution can also be avoided. The present process could be considered as a possible alternative to the Claus or LO-CAT process in which elemental sulfur is the only product losing valuable hydrogen energy.

Additionally, the liquid-phase H_2S oxidation process such as chelated iron-based process (LO-CAT) requires regeneration of spent solution by oxidation with air where air blower power consumption is one of the major operating costs (Kohl and Nielsen, 1997).

However, in the present process, this step is not required because the oxidizing agent (m-CNB) is being converted to value-added product (m-CA). The present process is, therefore, economically attractive from an industrial point of view.

Scope for future work

This chapter suggests the scope for further work based on the observations, results and conclusions drawn from the present study. The chapter has been organized to identify the areas where improvement that can be done on the same systems to get better conversion and selectivity and to get rid of some problems faced here. Also, how the present methodology can be used to explore more in the field of phase transfer catalysis has been discussed.

Investigation of Mechanistic Pathways

Identification and characterization of different ionic species present in both the phases during the reduction of nitroarenes by H_2S-rich aqueous alkanolamines needs a detailed study. This study will help to establish the reaction mechanism accurately, and then to perform kinetic modeling.

Finding out Effect of other Parameters

In the present study, toluene has been used as a solvent in most of the cases because it is cheap. The physical properties of organic solvent play an important role on the PTC reaction, not only by influencing the intrinsic organic reaction but also by affecting the transport properties of PTC and active catalyst species (QSQ and QSH).

Other types of solvents like chlrobenzene, n-heptane and dichloromethane can be tried out. Interfacial tension between the two phases is another important factor as the properties of the two liquid interface may influence the reaction regime and also PTC transport properties.

Use of Gas Streams Containing Other Gases along with H_2S

Most of the gas streams contain carbon dioxide (CO_2) as one of the major acid gas impurities. Therefore, the application of the present process for gas streams containing both H_2S and CO_2 largely depends on selectivity of the solvent towards H_2S. Extensive research is therefore needed in this field using various H_2S-selective solvents like aqueous methyldiethanolamine (MDEA) (Mandal et al., 2004; Bolhàr-Nordenkampf et al., 2004; Xu et al., 2002a) and MDEA in non-aqueous solvents like *N*-methyl pyrrolidone, ethylene glycol, etc. (Xu et al., 2002a, 2002b).

Although ammonia and MDEA was proved to be H_2S selective, it is almost impossible to get any solvent that is 100% selective towards H_2S. Therefore, some amount of CO_2 will always remain in the aqueous phase even in the case of H_2S selective solvent. Therefore, there is an urgent need for evaluating the effect of CO_2 on the reaction system for the successful application of present process to industrial gas streams.

Improvement in Statistical Modeling

Even though statistical modeling and analysis was found to give quite satisfactory results in terms of optimizing the process conditions, it did not help us to find kinetic parameters as statistical method (and software) that we have used uses only linear polynomial as model equation but there were many reactions which would not be linear in nature. If modification can be done to include all type of equation in statistical software (so that we can get model equation similar to that we encounter in kinetic analysis), we can get kinetic parameters and optimization simultaneously.

Exploring the Possibility of Single-pot Synthesis Using H_2S

In accordance with the present work, H_2S present in the gas streams can be utilized to produce value-added products in two steps, (1) Removal of H_2S from gas stream by ammonia and alkanolamine-based process (2) And production of value-added chemicals using H_2S-rich solution obtained from the first step. If it is possible to carry out this process in a single step (that is,

simultaneous removal of H_2S and chemical reaction in a single vessel), the economy of the whole process will improve greatly. Therefore, a detailed study is urgently needed in this direction.

Regeneration of Spent Ammonia/ Amine Solution

No focus has been given on the reuse of spent ammonia or amine solution after the reaction. Experiments need to be done to reuse the aqueous alkanolamine solution after separating it from organic phase. Regeneration is not required as after the reaction, the alkanolamine should contain less H_2S in either physically absorbed or chemically bound state. So, H_2S can be again passed through the contaminated (with PTC and other ionic salts) lean alkanolamine solution. Research is also required to see the efficiency of the contaminated lean amine to absorb further H_2S and then carrying out the desired reaction again.

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